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Abstract

Sulfamethoxazole (SMX) and sulfapyridine (SPY), two representative sulfonamide antibiotics, have gained increasing attention because of the ecological risks these substances pose to plants, animals, and humans. This work systematically investigated the removal of SMX and SPY by carbon nanotubes (CNTs) in fixed-bed columns under a broad range of conditions including: CNT incorporation method, solution pH, bed depth, adsorbent dosage, adsorbate initial concentration, and flow rate. Fixed-bed experiments showed that pH is a key factor that affects the adsorption capacity of antibiotics to CNTs. The Bed Depth Service Time model describes well the relationship between service time and bed depth and can be used to design appropriate column parameters. During fixed-bed regeneration, small amounts of SMX (3%) and SPY (9%) were irreversibly bonded to the CNT/sand porous media, thus reducing the column capacity for subsequent reuse from 67.9 to 50.4 mg/g for SMX and from 91.9 to 72.9 mg/g for SPY. The reduced column capacity resulted from the decrease in available adsorption sites and resulting repulsion (i.e., blocking) of incoming antibiotics from those previously adsorbed. Findings from this study demonstrate that fixed-bed columns packed with CNTs can be efficiently used and regenerated to remove antibiotics from water.

Keywords: antibiotics, nanotechnology, water treatment, filtration, removal efficiency

1. Introduction

Sulfonamide antibiotics are widely used as human and veterinary pharmaceuticals (Halling-Sørensen et al., 1998; Kolpin et al., 2002; Thiele-Bruhn, 2003). Sulfamethoxazole (SMX) and sulfapyridine (SPY) are two commonly used sulfonamide antibiotics primarily used for treating human patients, and are well known to bioaccumulate up the food chain and trigger acute as well as chronic adverse effects. (Göbel et al., 2005). Recent findings indicate that simultaneous exposure to multiple antibiotics could result in the enhanced toxic effects (Park and Choi, 2008). A general concern for public health is the development of antibiotic resistance from chronic exposure to antibiotic contaminated water. Therefore, it is urgent to investigate the pathways through which SMX and SPY disperse in the environment, and develop systems that can efficiently remove these dissolved substances from water.

Entry pathways of sulfonamide antibiotics to aquatic environments include aquaculture activity, pharmaceutical manufacturing, and medical waste disposal. Additionally, access could be indirectly gained to surface and subsurface waters from leached waste of livestock receiving antibiotic treatment (Baran et al., 2011). Precipitation events could further accelerate the release of antibiotics concentrated in animal manure, which, once dissolved in surface waters, could mix and load groundwater within the soil profile. The protection of surface and groundwater quality, as two primary sources for drinking water, from contamination of leached antibiotics is of great priority for pubic and environmental health.

A variety of physiochemical techniques have been developed to remove or destroy antibiotics from water sources, including oxidation (Beltrán et al., 2008), ion exchange

(Choi et al., 2007), reverse osmosis (Adams et al., 2002), and adsorption (Ternes et al., 2002). Adsorption is a standard method used to remove dissolved contaminants from water. Adsorbents, such as clay (Avisar et al., 2010), zeolite (Braschi et al., 2010), and activated carbon (Caliskan and Gokturk, 2010), have been examined for their removal efficiency of sulfonamide antibiotics in aqueous solutions. Solution chemistry has been shown to strongly affect the removal efficiency of these adsorbents with particular importance placed on solution pH (Lertpaitoonpan et al., 2009), ionic strength (Gao and Pedersen, 2005), and presence of competitive sulfonamide antibiotics (Gao and Pedersen, 2010).

Carbon nanotubes (CNTs), as novel sorbents, have gained increasing attention because of their exceptional sorbing properties. CNTs have hollow and layered structures with a characteristically large surface area, thus endowing CNTs with great potential for superior sorption capability (Wang et al., 2009). Previous studies have demonstrated high adsorption ability of CNTs to both heavy metals (Stafiej and Pyrzynska, 2007) and organic pollutants (Zhang et al., 2010). Investigations on the adsorption of sulfonamide antibiotics by CNTs have reported that removal efficiency varies according to the quantity of walls making up the CNTs as well as to chemical pre-treatment of the CNTs (Ji et al., 2009; Ji et al., 2010). Pretreatment of CNTs (e.g., by surface functionalization) is widely used to improve the dispersion of these nanoparticles in aqueous solutions (Tian et al., 2011). The introduction of functional groups also increases the ion-exchange capacity of the CNTs, thereby augmenting the number of available sites that can participate in electrostatic adsorption (Atieh et al., 2010). As such, functionalized CNTs

have been reported to exhibit greater potential for removing antibiotics from aqueous environments than pristine CNTs (Zhang et al., 2010).

The current application of CNTs for antibiotic removal from water has been restricted to batch sorption methods. Two key disadvantages of batch methods include difficulty to collect exhausted/spent adsorbents and interruptions incurred when integrated to existing continuous processes (Eckenfelder, 2000). For example, the in-situ removal of antibiotics in the environment (e.g., an agricultural field) requires a continuous flow setup to cope with the intermittent discharge of antibiotic-loaded runoff. It is thus necessary to develop and optimize CNT-enabled water treatment methods that take advantage of the large sorption capacity of CNTs in a setup that can be deployed in the field.

Unlike batch sorption systems, fixed-bed filters permit continuous flow and adsorption of antibiotics from solution; thus, opening a wealth of opportunities for *in situ* water treatment. The fixed-bed filters enabled by high performance adsorbents exploit the high sorption capacity of the adsorbent, while enabling the practicalities of continuous flow operation. Despite the above-mentioned benefits of fixed-bed systems and great sorption potential of CNTs (Tian et al., 2012b), to the authors' knowledge, the removal of antibiotics from aquatic environment using CNT-enabled fixed-bed columns has not been explored.

In this work, we used CNT-enabled fixed-bed column methods to investigate the removal of SMX and SPY from aqueous solutions under various conditions. Our overarching objective was to investigate the removal efficiency of SMX and SPY by CNTs in a fixed-bed system under various physicochemical conditions. The specific

objectives of the work were to (1) examine the removal of SMX and SPY from aqueous solutions by trickling antibiotic-contaminated water through a CNT/sand fixed-bed column under conditions of varying pH, CNT incorporation method, adsorbent dosage, bed depth, adsorbate initial concentration, and flow rate, and (2) evaluate the efficiency of regeneration of the fixed-bed columns for reuse.

2. Materials and methods

2.1. Bed materials and conditions

Functionalized multi-walled carbon nanotubes (CNTs) (Cheap Tubes Inc., Brattleboro, VT) and quartz sand were used as filter materials in the fix-bed columns. Three methods of CNT incorporation to the sandy medium were tested (layered, mixed, and deposited), bed depths tested ranged from 6 to 15 cm, and flow rates ranged from 1 to 2 mL min^{-1}. Chemical conditions tested for fixed-bed experiments were 3.0 to 9.0 pH, 10 to 40 mg adsorbent dosage, and 10 to 40 mg L^{-1} of antibiotic concentration.

CNTs were produced using a chemical vapor deposition method with nickel and magnesium catalysts. Subsequent functionalization was achieved with an acid mixture of concentrated sulfuric and nitric acids (3:1, v:v) to introduce carboxyl and hydroxyl functional groups to the nanotube surface (Zhang et al., 2011). A batch of the functionalized CNTs were used in the dry powder form (undispersed CNTs), while a second batch was dispersed in water to create a suspension of CNTs (dispersed CNTs). To make the dispersion, 16 mg of the synthesized CNT powder were dispersed in 1000 ml deionized water and subsequently sonicated for 30 minutes in a Misonix S3000 ultrasonicator (QSonica, Newtown, CT).

Thorough characterization of the CNTs for physiochemical properties was performed for the following properties. Surface area of undispersed CNTs was measured using the NOVA 1200 surface area analyzer (Quantachrome Instruments, Boynton Beach, FL), following the Brunauer–Emmett–Teller (BET) nitrogen adsorption method at 77 K. Point of zero charge (PZC) of the undispersed CNTs was determined using the mass titration method (Noh and Schwarz, 1990). Hydrodynamic diameter of dispersed CNTs was determined by dynamic light scattering with a Brookhaven ZetaPlus (Brookhaven Instruments Corporation, Holtsville, NY). CNT concentration in suspension was calibrated by measuring the total absorption of light at wavelengths of 255 nm using Evolution 60 UV-Vis Spectrophotometer (Thermo Scientific, Waltham, MA).

Quartz sand (Standard Sand & Silica Co., Davenport, FL) was sieved into 0.5 - 0.6 mm grain size and washed using deionized water (DI water). Basic properties and surface elemental compositions of the sand were reported previously by the authors (Tian et al., 2012a).

2.2. Antibiotics

Two sulfonamide antibiotics, sulfamethoxazole (SMX) and sulfapyridine (SPY) (99%, Sigma-Aldrich Co., St. Louis, MO), were used as adsorbates in the fixed-bed column experiments. Chemical structures and properties of SMX and SPY are reported in Table S1 (Supporting Information). Stock solutions of SMX/SPY were prepared (200 mg/L) and subsequently spiked with either 0.1 M KOH or HCl to adjust for desired pH (3.0 – 9.0) of the final solution. Antibiotic concentrations were determined by light absorption at wavelengths of 265 nm with a UV-Vis Spectrophotometer (Caliskan and

Gokturk, 2010). Lack of temporal change of concentration of SMX and SPY confirmed their stability for the duration of our experiments (data not shown).

2.3. Fixed-bed column experiments

Fixed-bed column experiments were used to investigate the removal of dissolved antibiotics from water in a CNT/sand fixed-bed system. A summary of the conditions tested is presented in Table 1, which includes CNT incorporation methods, pH, bed depth, adsorbent dosage, and adsorbate initial concentration, and flow rate.

An acrylic column of 2.5 cm in diameter and 15 cm height was used to contain the CNT/sand system, to which appropriate amount of CNTs (Table 1) were packed with 146.8 g of sand for all packing methods. Wet-packing of the porous medium was used in order to minimize layering of and air entrapment in the porous medium. The porosity of all the CNT/sand columns was approximately 0.40. A peristaltic pump was connected at the top of the column (inlet) to regulate the flow rate. Additionally, membranes with 50 μm pores (Spectra/Mesh, Spectrum Laboratories, Inc.) were used at the inlet and outlet of the column to distribute the flow over the cross-sectional area of the fixed-bed.

For the tested nanoparticle incorporation methods, CNTs were added to the sand medium by means of layering, mixing, or deposition (Tian et al., 2012b). For the CNT layered method, undispersed CNTs were incorporated to the system as a layer on top of the wet-packed sand column. For the CNT mixed method, undispersed CNTs were first mixed with sand and subsequently wet-packed into the column. For the CNT deposited method, the column was first wet-packed sand and a dispersion of CNTs injected through the column with a peristaltic pump (Masterflex L/S, Cole Parmer Instrument, Vernon

Hills, IL) in a downward flow direction for more than 10 h. Then, the influent was changed to DI water was for 2 h to elute suspended (not deposited) CNTs from the column. Effluent samples were collected at the outlet of the column with a fraction collector (IS-95 Interval Sampler, Spectrum Chromatography, Houston, TX) to monitor the concentration of eluted CNTs. Dispersed CNT concentration was determined by total absorption of light at wavelengths of 255 nm with UV-Vis Spectrophotometer. Mass balance calculations of injected and eluted CNTs were used to determine the amount of retained CNTs in the column. It is important to note that prior to use for antibiotic sorption experiments, no CNTs were detected in the effluent of the CNT/sand packed columns; therefore, CNT incorporation to the sandy medium considered irreversible. A column packed only with natural sand was used as the control.

After packing the column with the methods described above, an antibiotic-free background solution was injected to the column for 2 hr until the pore water chemistry reached equilibrium. Subsequently, an antibiotic solution was continuously injected to column and effluent samples collected at fixed intervals with a fraction collector. The concentration of antibiotics in the column effluent was then measured with UV-Vis Spectrophotometer and breakthrough curves built with this information. The experiment was terminated when the effluent concentration matched the initial concentration. All the column sorption studies were performed in duplicate.

2.4. Column regeneration and recycling

Spent fixed-bed columns (i.e., as resulted from antibiotic sorption tests described in the section prior) were used to evaluate bed regeneration and recycling efficiency.

Experimental conditions of the selected columns included: CNT incorporation by mixing, pH of 5.6, adsorbent dosage of 10 mg, bed depth of 15 cm, adsorbate initial concentration of 20 mg/L, and flow rate of 2 ml/min.

To regenerate the spent columns, a solution containing 30 g/L NaCl and 1.5 g/L NaOH of pH 12 was injected to the fixed-bed columns at the same flow rate as that used for antibiotic sorption experiments until effluent SMX or SPY concentrations fell below the detection limit (Faki et al., 2008). Effluent samples were collected and analyzed using the same protocol as that in the column filtration experiment. The column recycling was used to evaluate the viability of reuse of the CNT/sand fixed-bed column. After regeneration of the column and equilibration with background solution, column adsorption and sample analysis were performed under the same conditions. The column was recycled up to five times and column capacity at each reuse cycle determined. All the column regeneration and recycling studies were performed in duplicate.

3. Results and discussion

3.1. Column analyses

The two antibiotics showed very high mobility in the CNT-free fixed-bed filters (Figure 1), which can be attributed to their low reactivity with the sand media (Chen et al., 2011). Columns enabled with CNTs, however, showed high retention ability for both SMY and SPY (Figure 1), indicating that CNTs can be used in fixed-bed columns to remove antibiotics in solution. For all tested conditions, the CNT/sand fixed-bed column capacity ranged from 11.7 - 92.0 mg/g for SMX and 77.8 - 123.4 mg/g for SPY (Table 1).

The primary adsorption zone (PAZ) concept developed by Gupta et al (Gupta et al., 1997; Gupta et al., 2000) was used to analyze the breakthrough data of the antibiotics in the CNT/sand columns. During antibiotics injection into the fixed-bed column, the PAZ initially formed as a narrow band at the top of column. As column operation continues, the upper layers of the adsorbents (CNTs) become saturated with incoming antibiotics and the PAZ advances downward through the fixed-bed column until it reaches the bottom most layer of the column (Kundu and Gupta, 2005; Sousa et al., 2010). At this point, the injected antibiotics begin to breakthrough the column, as detectable in the effluent samples. In this work, normalized concentrations (C/Co) of antibiotics in the effluent were plotted against the operation time (min) to obtain the breakthrough curves of the antibiotics in the columns.

Parameters controlling the formation and movement of the PAZ can be quantitatively determined form the breakthrough data (Benefield et al., 1982; Kundu and Gupta, 2005). Definition of the PAZ parameters (e.g., t_b, t_e, v_z et al.) used in this study is provided in Table 2. These parameters were calculated to quantitatively assess the effect of pH (3.0, 5.6, 7.0, or 9.0), CNT incorporation method (layered, mixed, or deposited), adsorbent dosage (10, 20, 30, or 40 mg), bed depth (6, 9, 12, or 15 cm), adsorbate initial concentration (10, 20, 30, or 40 mg L^{-1}), and flow rate (1, 2, 3, or 4 mL min^{-1}), on the removal efficiency of CNT/sand columns to the two antibiotics. The determined PAZ and column adsorption parameters for all the experimental conditions tested are summarized in Table 1 and details provided in the supporting information (Tables S2-S7).

3.2. Effect of CNT incorporation method

The effect of CNT incorporation method on the adsorption and transport of SMX and SPY in the columns is illustrated in Figure 1. The column maximum adsorption capacities to SMX and SPY, defined as mg of antibiotic per g of CNTs, are summarized in Table 1. Experimental results indicate that the column adsorption capacity for SMX was 68.5 mg/g for layered method, 69.3 mg/g for mixed method, and 77.7 mg/g for dispersed method, with the capacity trend in the order of layered < mixed < dispersed. A similar performance in the CNT incorporation method was observed for experiments filtering SPY antibiotic. Likewise, the time to column exhaustion, t_e, (as reported in Table 1) indicates that CNT incorporation by the dispersed method prolongs antibiotic sorption time the most; thus, increasing the column's sorption capacity. As presented in the supporting information (Table S2), the time required for the PAZ to form, t_f, and time required for the PAZ to move through the fixed-bed, t_z, followed the same trend for the tested CNT incorporation methods. However, from a practical perspective the construction of a CNT-enabled fixed-bed column by the mixed CNT method is recommended with little compromise on the sorption performance of the system. Therefore, the remaining facets of the study are focused on fixed-bed systems built with the mixed CNT method.

3.3. Effect of pH

The effect of solution pH on the adsorption and transport of SMX and SPY in the columns is illustrated in Figure 2. Experimental results showed that the breakpoint time ,t_b, decreased from 33.4 to 16.6 min with the increase of pH from 3.0 to 9.0 (Table 1),

indicating that pH induced accelerated transport of SMX and SPY in the columns as conditions became more alkaline. As presented in the supporting information (Table S3), the inverse correlation between t_f and pH indicates that the PAZ formed faster at higher pH conditions. Similarly, shorter t_z and faster v_z with higher pH conditions indicate that PAZ forms and moves faster under these conditions. Table 1 shows that, when pH was increased from 3.0 to 9.0, the column adsorption capacity of SMX and SPY decreased from 84.9 to 11.7 mg/g and 93.9 to 77.8 mg/g, respectively. This suggests that alkaline pH dramatically decrease of the column ability to remove antibiotics, especially for SMX.

Mass titration measurements indicated that the PZC of CNTs was 2.2, signifying that the surface of CNT was negatively charged for all the treatments tested in the present study. The surface charge of SMX and SPY varied greatly with pH, as represented by the acidity constants (pK_{a1} = 1.8, pK_{a2} = 5.6 for SMX and pK_{a1} = 2.3, pK_{a2} = 8.4 for SPY). Table S1 in the Supporting Information provides the details of the speciation of SMX and SPY at the four solution pH values used this study. SMX and SPY became increasingly negatively charged with increasing solution pH; thus promoting electrostatic repulsion between CNTs and antibiotics. The larger fractions of neutral antibiotic species for SPY relative to those of SMX at the four pH levels tested explain well the observed differences in sorption capacity, by way of pH dependent speciation and its respective electrostatic phenomenon. For example, adsorption capacity at pH 7 for SPY was recorded at 86.1 mg g^{-1}, while that for SMX was 45.8 mg g^{-1}. The antibiotic speciation at the same pH was dominated by SMX^- (96%) or neutral SPY (96%), which is expected to exhibit different degrees of electrostatic repulsion when interacting with CNT surfaces. In

agreement with the antibiotic speciation effect, Figure 2 illustrates the large effect of pH on adsorption capacity of SMX when passing through the CNT/sand fixed-bed column, while a negligible effect is observed on adsorption capacity of SPY for identical experiments.

Beside the electrostatic phenomena described above, π-π interactions between functional groups are suspected to contribute to the adsorption of SMX and SPY by CNTs, as has been previously been implicated for sorption of phenolic compounds by CNTs (Lin and Xing, 2008). Amine functional groups and N-heteroaromatic rings in SMX and SPY are known to serve as π-acceptors; whereas, carboxyl and hydroxyl functional groups on benzene rings in CNTs can serve as both π-acceptors and π-donors (Zhang et al., 2010). Thus the authors propose that the attraction of acceptor-acceptor and acceptor-donor pairs between the antibiotics and the CNTs is an additional mechanism responsible for the observed strong adsorption of antibiotics onto CNTs at lower pH values.

3.4. Effect of bed depth

The effect of bed depth on the adsorption and transport of SMX and SPY in the columns is illustrated in Figure 3. The column adsorption capacities at various bed depths were in general greater for SPY (91.9 to 97.1 mg g^{-1}) than for SMX (69.3 to 72.8 mg g^{-1}) (Table 1).

To evaluate the effect of bed depth on the breakthrough time, the breakthrough data were interpreted using the Bed Depth Service Time (BDST) model. The BDST model was first introduced by (Bohart and Adams, 1920) and further developed by (Hutchins,

1973). This model has primarily been used in the analysis of fixed-bed breakthrough data of heavy metals (Ko et al., 2000; Cortes-Martinez et al., 2009) and organic pollutants (Abu-Lail et al., 2010; Patel and Vashi, 2012). The relationship between service time and bed depth is as follows:

$$t = \frac{N_0}{C_0 v} h - \frac{1}{k C_0} ln\left(\frac{C_0}{C_t} - 1\right) \quad (1)$$

where t is the service time at breakthrough [min], N_0 is the dynamic adsorption capacity of the bed [mg L^{-1}], C_0 is the influent antibiotics concentration [mg L^{-1}], v is the linear flow velocity of feed to the fixed-bed [cm min^{-1}], h is the CNT/sand bed depth [cm], k is the adsorption rate constant [L mg^{-1} min^{-1}], and C_t is the effluent solute concentration at time t [mg L^{-1}].

The linear relationship between t and h (Figure 4) was described by the slope $\frac{N_o}{C_o n}$ and the intercept $\frac{1}{k C_0} ln\left(\frac{C_0}{C_t} - 1\right)$. The values of N_0 and k were thereafter back calculated. The critical bed depth, h_0, is the minimum depths of CNT/sand required to achieve the effluent breakthrough, which can be calculated from the lines best fitting equations by letting t = 0 (Kundu and Gupta, 2005; Mohan and Sreelakshmi, 2008).

The BDST model was developed for breakpoint, t_b, and exhausted point, t_e, respectively. Plots of bed depth against service time are presented in the Figure 4 with their respective linear regression. The excellent regression results ($R^2 > 0.9$) permit the fitted curves to be used for predicting the service time corresponding to a given bed depth both for SMX or SPY. Moreover, the identified relationship between bed depth and service time points out that changes in t_b are paralleled by changes in t_e; thus indicating

that the time required for the PAZ to move the length of its own height, t_z, is independent of bed depth. The horizontal distance between the two parallel lines of Figure 4 is taken as the height of the exchange zone (Kundu and Gupta, 2005), resulting in heights of 4.5 and 5.2 cm for SMX and SPY, respectively.

The additional BDST parameters N_0, k and h_0 were then calculated using the estimated regression values for breakpoint at different bed depths. Values of N_0, k, and h_0 for SMX were estimated at 16.58 mg L^{-1}, 0.038 L mg^{-1} min^{-1}, and 1.81 cm; while for SPY estimated values were of 20.72 mg L^{-1}, 0.023 L mg^{-1} min^{-1}, and 2.42 cm, These BDST parameters suggest that the removal ability of CNTs for SPY is better than that for SMX under the same conditions. For up-scaling of CNT/sand fixed-bed systems, the BDST model could be used to optimize the design and performance of large-scale fixed-bed columns for the removal of antibiotics from water (Mohan and Sreelakshmi, 2008).

3.5. Effect of adsorbent dosage

The effect of adsorbent dosage on the adsorption and transport of SMX and SPY in the columns is illustrated in Figure S1 (Supporting Information). As expected, the breakpoint time, t_b, increased with the increase in CNT dosage. As reported in Table 1, a four-fold increase of CNT in the column ensued an increase in t_b from 27.5 to 66.5 min for SMX and 33.5 to 85.5 min for SPY. Conversely, the column adsorption capacity decreased from 69.3 to 62.8 mg/g for SMX and 91.9 to 82.4 mg/g for SPY for the same increase in CNT dosage. From a fixed-bed capacity standpoint, it is clear that the mass of adsorbed antibiotics per unit mass of CNTs decreased with greater amount of CNTs in the fixed-bed, thus reducing the performance efficiency of the fixed-bed filter. A possible

explanation for the decrease in fixed-bed efficiency could be attributed to π-bond interference of the additional CNTs with each other; thus preventing the formation of π-bonds between antibiotics and the CNTs in the column (Ozdemir et al., 2009; Montazer-Rahmati et al., 2011).

3.6. Effect of adsorbate initial concentration

The effect of adsorbate initial concentration on the adsorption and transport of SMX and SPY in the columns is illustrated in Figure S2 (Supporting Information). As shown in the figure, the breakpoint time was shortest with the highest SMX and SPY initial concentration, and increased as initial concentration decreased. The breakpoint time decreased from 37.5 to 25.5 min for SMX and 51.5 to 25.5 min for SPY as the initial concentration of antibiotics quadrupled. The column adsorption capacity of antibiotics by CNT was increased from 54.8 to 92.0 mg g^{-1} for SMX and 80.9 to 123.4 mg g^{-1} for SPY for the same increase in antibiotic initial concentration (Table 1). This large increase in fixed-bed capacity is ascribed to the larger concentration gradient generated that promotes greater mass transfer of antibiotics from the liquid phase to the solid phase (i.e., the CNT surface) (Nasuha et al., 2010).

3.7. Effect of flow rate

The effect of flow rate on the adsorption and transport of SMX and SPY in the columns is illustrated in Figure S3 (Supporting Information). As shown in the figure, the breakpoint time decreased with increasing flow rates from 59.1 to 14.8 min for SMX and 67.1 to 16.8 min for SPY (Table 1). The column removal capacity of antibiotics by CNT

was decreased from 78.3 to 61.9 mg g^{-1} for SMX and 94.9 to 83.6 mg g^{-1} for SPY when flow rate was increased from 1 to 4 ml min^{-1}. This reduction in sorption capacity is likely due to the decrease in contact time between the antibiotics and CNTs at higher flow rates. The increase of flow rate also accelerates the movement of PAZ downwards in the fixed-bed, which contributes to decreased adsorption capacity and column efficiency (Ozdemir et al., 2009).

3.8. Column regeneration and recycling

The release curves of SMX and SPY in the post-adsorption columns during the regeneration process are presented in the supporting information (Figure S4). Results showed that the release of SMX and SPY produced a maximum effluent concentration of 1.2 C/C_0 after 22 min of regeneration treatment. The mass recovery for the regeneration process was 97% for SMX and 91% for SPY, suggesting that 3% of SMX and 9% of SPY of the previously sorbed antibiotics were strongly and irreversibly bonded to the CNT/sand porous media at each regeneration cycle. Thus, although the sorption capacity of the fixed-beds diminished after each adsorption-regeneration cycle, the fixed-beds continued to have an acceptable capacity to remove antibiotics from contaminated waters.

The change of column capacity for 5 consecutive regeneration cycles for each antibiotic are presented in Figure 5. From these plots it is evident that column capacity decreased after reuse from 67.9 to 32.6 mg g^{-1} for SMX and from 91.9 to 40.0 mg g^{-1} for SPY. As suggested previously, the reduced column capacity could be a result of decreased available adsorption sites (i.e., blocking) and repulsion by the irreversibly sorbed antibiotics from previous cycles. It is important to note that although the absolute

sorption capacity of the CNT-sand fixed-beds is lower for SMX than for SPY on a mg g^{-1} basis, regeneration of the columns after 5 cycles reduced the sorption capacity of both antibiotics by a similar fraction (52% for SMX and 56% for SPY).

4. Conclusions

The removal of sulfamethoxazole (SMX) and sulfapyridine (SPY) from aqueous solutions by fixed-bed columns was tested under various conditions. Experimental results indicate that, from the multiple factors that can be varied in a fixed-bed filtration system (CNT incorporation, pH, bed depth, adsorbent dosage, adsorbate initial concentration, and flow rate), the effect of pH affects column adsorption capacity most strongly. The mechanism driving this phenomenon were attributed to the speciation of negative, neutral and positive antibiotics molecules at the tested pH levels, the level of protonation the functional groups on the CNT surfaces, and on possible π-bonds between the adsorbant and adsorbate. Of the three CNT incorporation methods tested, columns built with dispersed CNTs rendered the columns with a greater adsorption capacity than those built with undispersed CNTs due to the greater CNT surface area within the column. The Bed Depth Service Time (BDST) model describes well the relationship between service time and bed depth and further permits estimation of optimum column parameters. The increase of adsorbent dosage slightly decreases the capacity of the filters while extending the lifetime of the filter, but penalizes fixed-bed efficiency. Higher adsorbate initial concentration offers greater mass transfer driving force to move antibiotics in the liquid phase towards the CNTs surface; thus, enhancing the efficiency of antibiotic sorption. The increase of flow rate results in the decrease of contact time between the antibiotics

and CNTs. This accelerates the movement of PAZ downwards in the fixed-bed prior to becoming saturated, thus contributing to the overall decrease in adsorption capacity. Regeneration of the fixed-beds was successfully achieved, demonstrating that only a small fraction of SMX and SPY were irreversibly sorbed onto the CNT/sand porous medium. As a result, each regeneration cycle reduced the capacity of the bed by 8-26% for both types of antibiotics, but permitted the column to be reused multiple times with an acceptable antibiotic sorption capacity. With recent capacity scale-ups driving prices down ($25-38 per kg) (Agboola et al., 2007), operational cost for CNTs in wastewater treatment could be lower than other commercial carbon sorbents, such as activated carbon (AC). It has been pointed out that CNTs are better adsorbents to antibiotics than some of the ACs under many circumstance (Pan and Xing, 2008).

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Figure Captions

Figure 1. Breakthrough curves of sulfamethoxazole (SMX) and sulfapyridine (SPY) in the CNT/sand fixed bed columns under various CNT incorporation methods. Constant conditions included: pH 5.6, 10 mg CNTs, 15 cm bed depth, adsorbate initial concentration of 20 mg/L, and 2 mL/min flow rate.

Figure 2. Breakthrough curves of sulfamethoxazole (SMX) and sulfapyridine (SPY) in the CNT/sand fixed bed columns under various pHs. Constant conditions included: CNT incorporation by mixed method, 10 mg CNTs, 15 cm bed depth, adsorbate initial concentration of 20 mg/L, and 2 mL/min flow rate.

Figure 3. Breakthrough curves of sulfamethoxazole (SMX) and sulfapyridine (SPY) in the CNT/sand fixed bed columns under various bed depths. Constant conditions included: CNT incorporation by mixed method, pH 5.6, 10 mg CNTs, adsorbate initial concentration of 20 mg/L, and 2 mL/min flow rate.

Figure 4. Bed Depth Service Time (BDST) model for (A) sulfamethoxazole (SMX) and (B) sulfapyridine (SPY) at breakpoint (C/C_0 = 5%) and exhausted point (C/C_0 = 95%). Constant conditions included: CNT incorporation by mixed method, pH 5.6, 10 mg CNTs, adsorbate initial concentration of 20 mg/L, and 2 mL/min flow rate.

Figure 5. Relationship between changes in column capacity (mg/g) of (A) sulfamethoxazole (SMX) and (B) sulfapyridine (SPY) for 5 fixed-bed regeneration cycles. Sorption conditions were conducted consistently for mixed CNT incorporation, at pH 5.6, 10 mg CNT, 15 cm bed depth, adsorbate initial concentration of 20 mg/L, and 2 ml/min flow rate.

Figure 1

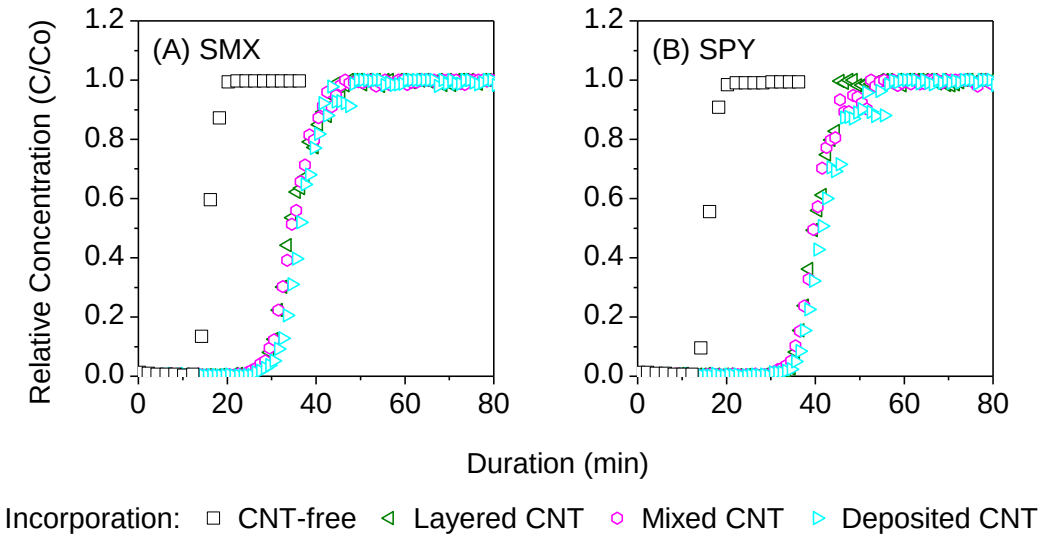


Figure 2

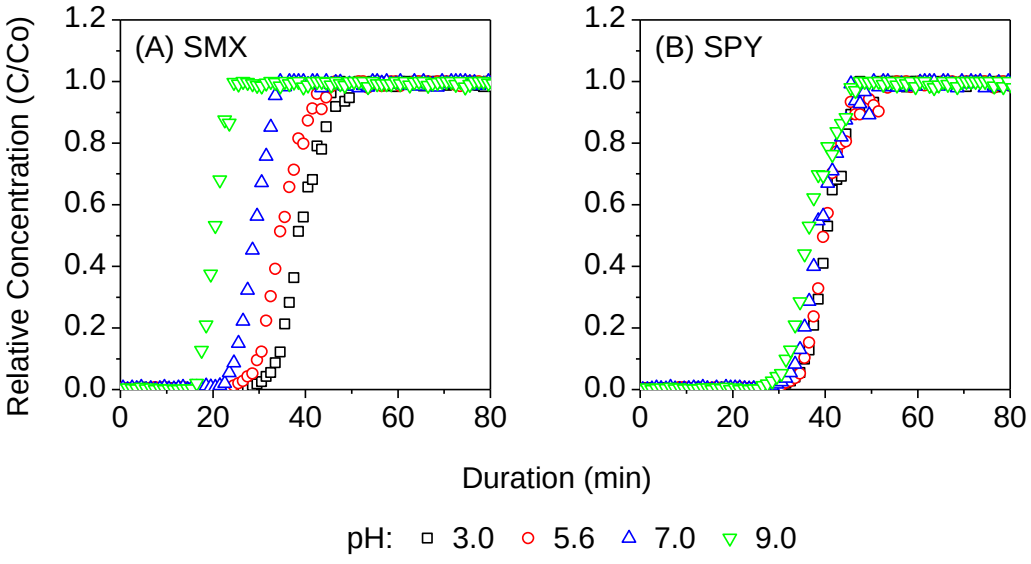


Figure 3

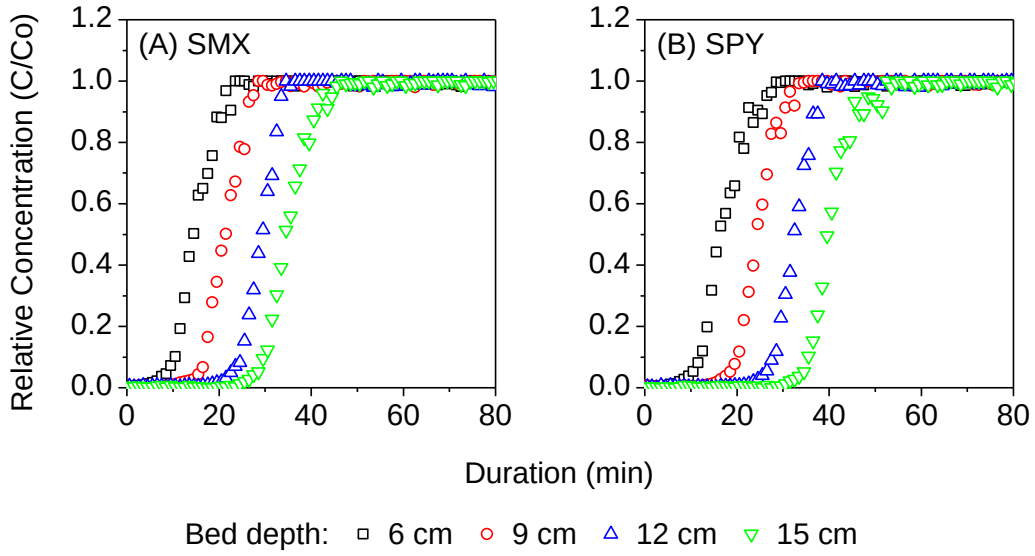


Figure 4

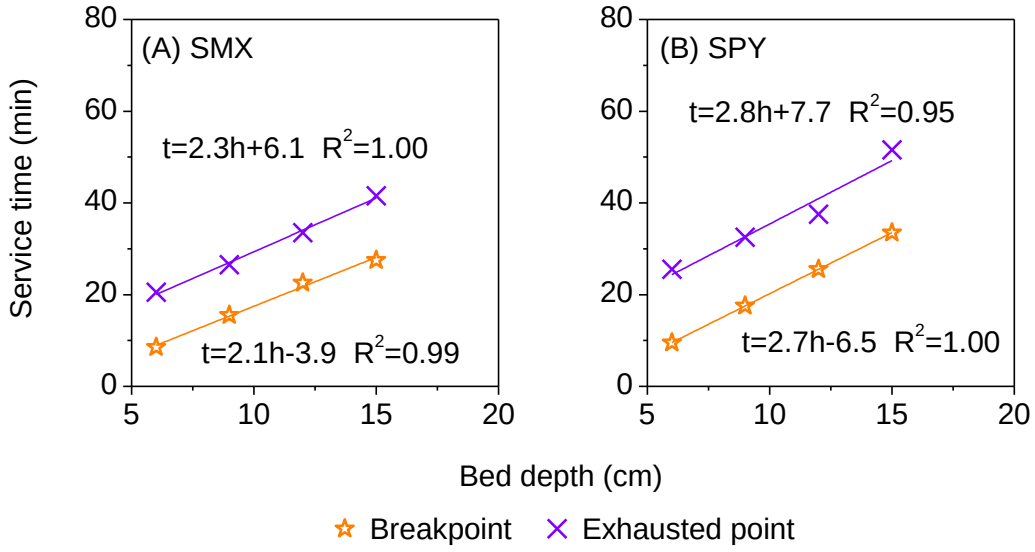
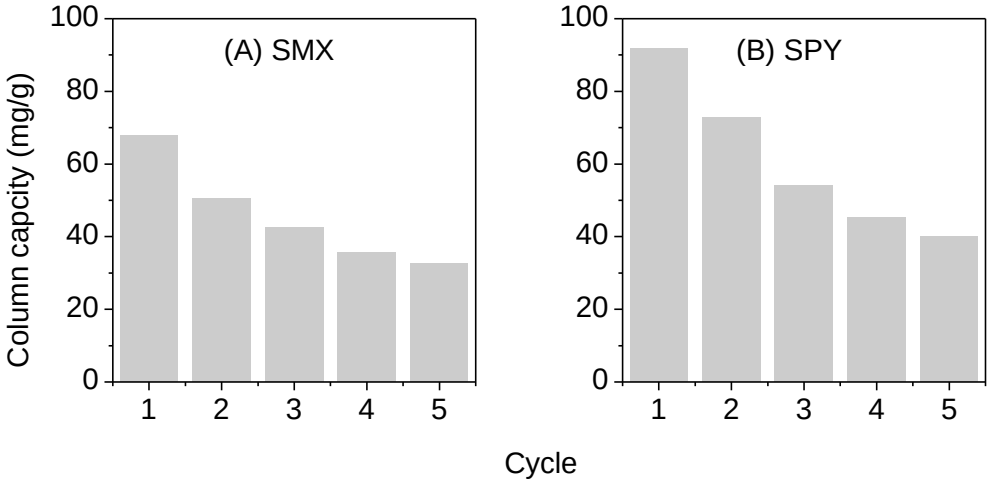


Figure 5



Tables

Table 1. Summary of transport and adsorption parameters of the two antibiotics in CNT/sand columns [(1)].

Treatment	SMX				SPY			
	t_b (min)	t_e (min)	v_z (cm/min)	Capacity (mg/g)	t_b (min)	t_e (min)	v_z (cm/min)	Capacity (mg/g)
Incorporation								
Layered	28.5	43.5	0.42	68.5	34.5	44.5	0.37	89.4
Mixed	27.7	44.5	0.43	69.3	33.6	51.5	0.37	91.9
Deposited	29.6	47.5	0.41	77.7	35.4	55.4	0.35	97.8
pH								
3.0	31.7	49.7	0.38	84.9	33.4	50.4	0.36	93.9
5.6	27.6	44.5	0.43	69.3	33.5	51.5	0.37	91.9
7.0	22.6	32.7	0.53	45.8	31.6	49.3	0.39	86.1
9.0	16.6	23.5	0.76	11.7	29.5	44.6	0.40	77.8
Bed depth								
6 cm	8.5	20.6	0.39	72.8	9.5	25.5	0.34	97.1
9 cm	15.5	26.5	0.41	71.6	17.5	32.5	0.36	94.5
12 cm	22.5	33.6	0.41	76.9	25.6	37.7	0.37	94.7
15 cm	27.4	44.5	0.42	69.3	33.6	51.8	0.37	91.9
Adsorbent dosage								
10 mg	27.5	44.6	0.42	69.3	33.5	51.3	0.37	91.9
20 mg	45.4	62.3	0.28	70.0	53.3	73.9	0.24	86.8
30 mg	58.3	76.9	0.23	64.9	70.4	101.3	0.18	85.1
40 mg	66.7	95.4	0.19	62.8	85.8	122.8	0.15	82.4
Adsorbate C_0								
10 mg/L	37.4	53.5	0.33	54.8	51.8	62.4	0.26	80.9

20 mg/L	27.4	44.5	0.42	69.3	33.7	51.4	0.37	91.9
30 mg/L	26.6	37.5	0.48	84.8	25.5	46.8	0.42	109.6
40 mg/L	25.6	32.5	0.52	92.0	25.5	41.5	0.45	123.4
Flow rate								
1 ml/min	59.3	93.5	0.20	78.3	67.0	103.2	0.18	94.9
2 ml/min	27.7	44.7	0.43	69.3	33.6	51.3	0.37	91.9
3 ml/min	19.8	27.7	0.65	67.7	22.3	29.7	0.55	90.2
4 ml/min	14.8	19.9	0.91	61.9	16.8	21.7	0.79	83.6

(1) The parameters include breakpoint time (t_b), exhausted time (t_e), adsorption zone velocity (v_z), and column capacity.

Table 2. Definition and formula of the primary adsorption zone (PAZ) parameters used in this study.

Parameter	Unit	Definition	Formula
h	cm	Bed depth	
C_0	mg/L	Influent antibiotic concentration	
C_t	mg/L	effluent antibiotic concentration at time t during the experiment	
t_b	min	Breakpoint time when the normalized effluent concentration (C/C_0) reaches 5%	
t_e	min	Time when C/C_0 reaches 95%, also defined as the time when the column is exhausted/spent	
t_z	min	Time required for the PAZ to move through the fixed-bed column after it has become established	$t_z = t_e - t_b$
F	-	Fraction of the PAZ that still capable of adsorption (i.e., unspent adsorbent fraction in the PAZ)	$F = \frac{\int_{t_b}^{t_e}(1-\frac{C_t}{C_0})\,dt}{t_e - t_b}$
t_f	min	Elapsed time between initial injection and the breakpoint, also defined as the time required for the initial formation of the PAZ	$t_f = (1-F)t_z$
v_z	cm/min	Velocity of PAZ progressing through the bed	$v_z = \frac{h}{t_e - t_f}$
h_z	cm	Height of the adsorption zone	$h_z = v_z t_z$
s	-	Saturation percentage of the total column at breakthrough	$s = \frac{h + (F-1)h_z}{h} \times 100$